Journal of Ceramic Processing Research. Vol. 12, No. 5, pp. 493~495 (2011)

J O U R N A L O F
Ceramic Processing Research

Characterization and properties of $BaTiO_3$/MgO nanocomposite ceramics

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In this research, $BaTiO_3$/xMgO nanocomposite ceramics, where x = 0, 0.3, 0.5, 0.7 and 1.0 vol%, were prepared by a mixed-oxide method. The effect of MgO additions on the phase formation, microstructure and dielectric properties of this system was investigated via X-ray diffraction (XRD), scanning electron microscopy (SEM) and dielectric spectroscopy, respectively. From the results, XRD analysis showed that there is no unwanted phase except $BaTiO_3$ and MgO observed in these ceramics. Abnormal grain growth was found in pure $BaTiO_3$ ceramic with a 75.32 μm average grain size. After adding MgO nanoparticles into the system, the grain size significantly decreased to 0.55 μm and continuously decreased with increasing MgO content. For the dielectric properties, the pure BT ceramic exhibits a sharp and high dielectric peak whereas a low and broad peak is found in BT/MgO nanocomposite ceramics, which can be explained by the composite structure.

Key words: Barium Titanate, magnesium oxide, Nanocomposite, Dielectric property.

Introduction

Barium titanate ($BaTiO_3$) with a perovskite structure is a strong dielectric material which has far reaching applications in the electronics industry for transducers, actuators and high-k dielectrics and is mostly used to make multilayer ceramic capacitors (MLCC) [1, 2]. Many previous studies [3, 4] reported that the dielectric and ferroelectric properties of $BaTiO_3$ can be efficiently controlled by adding dopants. Magnesium oxide (MgO) is one of the basic doping materials in $BaTiO_3$-based MLCC. Moreover, MgO together with rare earth elements, such as La, Sm, Dy, Ho and Er, are widely used to achieve an X7R application and to develop reduction-resistant $BaTiO_3$-based MLCC with Ni electrodes in the requirement of miniaturization, large capacitance and cost reduction [4-6]. Furthermore, Mg ions are also reported to play an important role in inhibiting the grain growth of $BaTiO_3$. Hwang *et al.* [4] studied the effect of Er_2O_3 and MgO additions on the dielectric properties of $BaTiO_3$ ceramics in a reduced atmosphere and reported that MgO effectively prevented the material from being reduced and suppressed grain growth. Their work also exhibited that an X7R material with a moderate temperature dependence can be developed by the addition of MgO with higher than 2.0 mol% Er_2O_3 to $BaTiO_3$. Although, numerous studies have been made on the co-doping effects of MgO and rare-earth oxides on the microstructure and properties of $BaTiO_3$-based system, there are only a few papers on the properties of MgO-doped $BaTiO_3$ ceramic.

Currently, since nanoscience and nanotechnology have been proposed in the field of electroceramics, the addition of nanometre sized particles has successfully engineered the microstructure and improved properties of various ferroelectric materials. $BaTiO_3$-based ceramics incorporating nano-particles such as Al_2O_3, SiC, NiO, MoO_3 and WO_3 have been studied [7, 8]. Their results showed that the mechanical and electrical properties of $BaTiO_3$ can be improved by nano-particle additions. Therefore, the purpose of this study was to fabricate $BaTiO_3$ ceramic with small amounts of nano-sized MgO particles added by a conventional process. The effect of MgO nanoparticles on the phase formation, microstructural evolution and electrical properties of $BaTiO_3$ ceramic will be investigated.

Experimental Procedure

$BaTiO_3$/xMgO nanocomposite ceramics, where x = 0, 0.3, 0.5, 0.7 and 1.0 percent by volume, have been fabricated from $BaTiO_3$ powder and MgO nanoparticles employing a conventional mixed oxide method. Firstly, $BaTiO_3$ (or BT) powder was synthesized from reagent grade $BaCO_3$ and TiO_2 precursors (Aldrich, > 99% purity). After ball-milling for 24 h in ethyl alcohol, the slurry was dried at 120 °C and calcined at 1250 °C for 2 h in a closed alumina crucible. After that, MgO nanoparticles

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were weighed and mixed with the BT powder by ball milling for 24 h to form various compositions. The mixed BT/MgO powders were then pressed to pellets 10 mm in diameter and 0.8 mm in thickness using uniaxial die pressing. The green bodies were sintered for 2 h over a range of temperatures between 1300 to 1450 °C depending upon the composition. Densities of the sintered ceramics were measured by the Archimedes method and X-ray diffraction (XRD using CuK_α radiation) was employed to identify the phases formed. The grain morphology and size were directly imaged using scanning electron microscopy (SEM) and the average grain size was determined using a mean linear intercept method. For electrical measurements, silver paste was painted on both sides of the polished pellets as the electrodes. The dielectric properties of the sintered ceramics were studied as a function of temperature. The capacitance was measured with a HP4284A LCR meter in connection with a chamber capable of high temperature measurement. The dielectric constant (ε_r) was calculated using the geometric area and thickness of the discs.

Results and Discussion

The phase formation behavior of $BaTiO_3$ ceramic with small amount of nano-sized MgO particles added is revealed by XRD as shown in Fig. 1. The diffraction pattern of BT ceramic ($x = 0.0$) matches exactly with tetragonal perovskite $BaTiO_3$ in the JCPDS file no. 75-0460, with lattice parameters $a = 3.9945$ Å and $c = 4.0335$ Å and space group P4mm (no.99). In the patterns, there are no extra peaks representing any secondary phases. Increasing the MgO content gradually leads to a lower lattice volume as indicated by the XRD peaks shifting towards higher angles (or lower d values) [9].

Fig. 2 shows microstructures of as-fired $BaTiO_3$/MgO ceramics sintered at 1400 °C with various MgO contents.

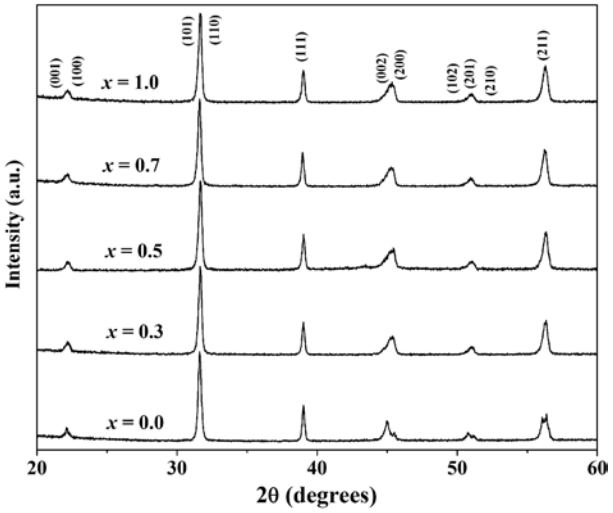

Fig. 1. XRD diffraction patterns of $BaTiO_3$/MgO nanocomposite ceramics sintered at 1400 °C.

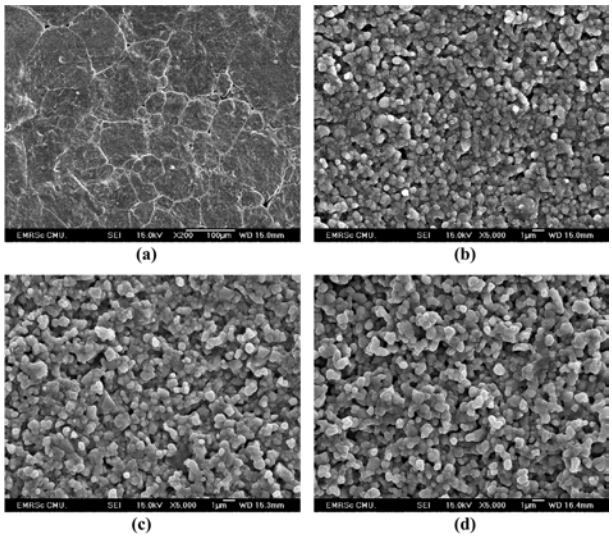

Fig. 2. SEM micrographs of $BaTiO_3$/xMgO nanocomposite ceramics: (a) $x = 0.0$, (b) $x = 0.3$, (c) $x = 0.5$ and (d) $x = 0.7$.

The average grain sizes of all the ceramics was determined by the linear intercept method using SEM micrographs and are listed in Table 1. Typical microstructures of pure BT ceramic prepared by a conventional mixed oxide method similar to previous workers [10, 11] were observed. A considerable homogeneity of the microstructure with abnormal grain growth (very large grains up to 100 μm in diameter) was revealed. The average grain size of the pure BT ceramic is about 75.32 μm. This could be attributed to a recrystallization mechanism during solid state sintering and also a deviation from stoichiometric compositions derived from mixed oxide route. After mixing with MgO nanoparticles, it can be clearly seen that the grain size significantly decreases to 0.55 μm and continuously decreases with increasing MgO content (as shown in Table 1). Previous studies [12, 13] reported that MgO was detected in the grain boundary regions of the system, which might act as a grain growth inhibitor. Therefore, these MgO or related compounds existing in the grain boundaries might be the reason for the fine grain size in BT/MgO ceramics. However, these phases could not be detected by XRD analysis due to the small amount of MgO. Furthermore, the bulk density of BT/MgO ceramics are also shown in Table 1 as a function of MgO content. It seems that the density slightly decreases with increasing MgO. It can be assumed that the MgO addition in the grain boundary regions suppresses the grain growth during the sintering process, resulting in poor densification of the ceramics.

The change in dielectric constant of BT/MgO nanocomposite ceramics as a function of MgO content over the temperature range from 30-160 °C measured at 1 kHz is shown in Fig. 3. A sharp dielectric peak at the Curie point (T_C) ~128 °C is observed in the pure BT ceramic and the dielectric constant (ε_r) reaches up to 5776. After adding 0.3 vol% MgO into the system, it is found that dielectric peak becomes broader and the ε_r value

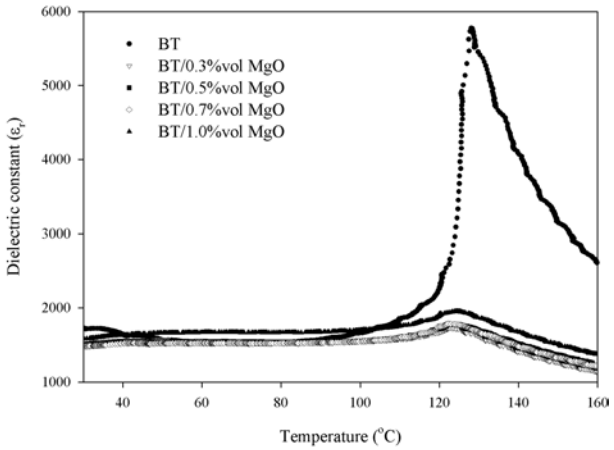

Fig. 3. Temperature dependence of the dielectric constant of $BaTiO_3$/MgO nanocomposite ceramics measured at 1 kHz.

Table 1. Characteristics of $BaTiO_3$/MgO ceramic nanocomposites

MgO content (vol%)	Density (g/cm^3)	Average grain size (μm)	T_C (°C)	ε_r
0	5.8261	75.32	128	5776
0.3	5.7228	0.55	122	1730
0.5	5.6560	0.44	124	1780
0.7	5.6300	0.41	122	1785
1.0	5.6595	0.40	124	1956

significantly drops to 1730. With a further increase in the MgO content, ε_r swings in the same range. Moreover, the Curie temperatures of BT/MgO ceramics also show the same trend and the dielectric data of all samples are listed in Table 1. There are various proposals for explaining of the dielectric response of composite materials. Ausloos [14] studied the effective dielectric constant theories of composite solids. His work reported that a broad spectrum of the dielectric constant is the result of a clustering effect, the shape of particles (or clusters) effect and a particle heterogeneity effect. In this study, it is possible that the low and broad dielectric peak of ceramics after adding MgO nanoparticles can be related to the composite structure. From the results of the microstructure and density data which suggested that this system might contain an excess of MgO or related compounds existing in the grain boundary regions, it is believed that a small amount of MgO did not dissolve into the $BaTiO_3$. Some of the MgO addition is thus present in the form of second phase inclusions in the $BaTiO_3$ matrix and located in the $BaTiO_3$ grain boundaries. These secondary phases may hinder domain wall motion sufficiently to reduce the dielectric constant.

Conclusions

The effect of MgO additions on the phase formation, microstructure and dielectric property of $BaTiO_3$ ceramic has been studied. X-ray diffraction could not detect any secondary phase, only pure $BaTiO_3$. The grain size of ceramics in this system strongly depends on the MgO content. The average grain size of pure $BaTiO_3$ is 75.32 μm, whereas that of $BaTiO_3$/MgO ceramics is about 0.5 μm. The fine grain size in BT/MgO ceramics might be caused by MgO or related compounds existing in the grain boundary regions which leads to grain growth suppression during the sintering process and results in poor densification of the ceramics. For the dielectric data, the dielectric constant (ε_r) of high density $BaTiO_3$ reaches to 5776 at T_C ~128 °C. After adding MgO nanoparticles to $BaTiO_3$, the e_r value significantly decreases. The dielectric behavior of $BaTiO_3$/MgO ceramics can be explained by the response theory of composite materials. It is believed that the MgO additions are present in the form of second phase inclusions in the $BaTiO_3$ matrix and located in the $BaTiO_3$ grain boundaries which may hinder domain wall motion sufficiently to reduce the dielectric constant.

Acknowledgements

This work is supported by the Thailand Research Fund (TRF), the Commission on Higher Education (CHE), the Young Scientist and Technologist Programme (YSTP), Faculty of Science and Graduate School of Chiang Mai University.

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